TECHNICAL SUMMARY REPORT

TO

ADVANCED RESEARCH PROJECTS AGENCY

ON

MATERIALS PREPARATION AND CHARACTERIZATION RESEARCH

For the Period 1 July 1970 to 31 December 1970

Contract No. DA-49-083 OSA 3140

ARPA Order No. 338, Amendment 5

THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

UNIVERSITY PARK, PENNSYLVANIA

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Part 1: INTRODUCTION

1.1 FORMAT

This semi-annual report reports only the work supported under the ARPA contract dealing with "Materials Preparation and Characterization." The Annual Report of the Laboratory issued at the end of the fiscal year reports both the ARPA work as well as all other research on materials carried out by the faculty of the Materials Research Laboratory. The scope of this report is therefore considerably narrower than that of the Annual Report, while at the same time it generally contains more detail than the latter.

Parts 2, 3, and 4 of this report summarize the results from the respective research areas of Glass Studies, Materials Preparation, and Materials Characterization.

1.2 SUMMARY OF HIGHLIGHTS

(a) Glass Studies

Some of our basic work on glass is finding its way into major applied programs of making ultrahomogeneous glass by the so-called "sol-gel" technique at Philips in Holland and Owens-Illinois here. We are now in the process of finishing up some work to determine the feasibility of a completely different route to "glass" making without ever melting the composition.

One of our most important results impinging on the chalogenide memory glass-switches is the fact that we have established that sputtered NCS films are very substantially different from regular glasses of the same composition

including the difference that the former often crystallize in two stages. Finally in the area of glass-science, we have found indications of invaluable use of (laser-) Raman spectroscopy in some universally important glass problems: e.g. the detection of incipient crystallization and understanding the boron-anomaly.

(b) Materials Preparation

In the materials preparation area, good progress on structural and crystal growth parameters for the ferroelectric detector and energy storage bismith titanate family has been made.

Also the initiation and installation of the vapor-growth methods is proceeding very well. Our objective here is to be able to grow ultrapure crystals of the simple oxides, specifically in the near future of CdO and NiO. Some very fine crystals fo CdO (max. 150 mm^3) have already been made and we are confident that by the end of the next period we will have such a unique (in the U.S.) facility and crystals of these two materials.

(c) Materials Characterization

In the characterization area after many painstaking years the precision work on double crystal x-ray spectrometry has borne fruit - some of it quite spectacular. Thus we are able to determine dislocation densities on the one hand, and piezoelectric coefficients on the other by a sirple x-ray method.

1.3 DISSEMINATION OF RESULTS AND PUBLICATIONS

Besides the usual presentation of papers by the Faculty at various national and international scientific meetings, we continue to make special efforts by non-routine methods to convey recent research results to industry and other interested parties. In one such venture we cooperated recently with Carnegie-Mellon University under NSF sponsorship in bringing together a "working party" on ultrahard materials. These will again be described in detail in the Annual Report.

Articles published or accepted for publication during the reporting period are listed below:

Bhalla, A., S. K. Suri and E. W. White, Crystallographic Polarity of Gel Grown β-AgI Crystals, J. Appl. Phys. (to be published Mar. 1971).

Bhalla, A. and E. W. White, Crystallographic Polarity Determination of γ-CuI, Acta Cryst. (to be published, 1971).

Ehman, M. F., and M. P. O'Horo, A Thinning Etchant for Cadmium Fluoride, J. Appl. Phys. (to be published Feb. 1971).

Garner, R. W. and W. B. White, Growth of Cinnabar (HgS) from Sodium Sulfide-Sulfer Fluxes, J. Cryst. Growth 7, 343 (1970).

McCarthy, G. J.,Divalent Europium Compounds in the System Eu-Mo-O and Eu-W-O. Mat. Res. Bull. 6, 31 (1971).

McCarthy, G. J. and W. B. White, On the Stabilities of the Lower Oxides of the Rare Earths. J. Less-Common Metals 22, 409 (1970).

Roy, D. M. and S. P. Faile, Experimental Introduction of Excess Ar^{40} into a Granitie Melt; Discussion of Paper by W. S. Fyfe, M. A. Lanphere and G. B. Dalrymple, Contr. Mineral and Petrol. 27, 258 (1970).

Suri, S. K., and H. K. Henisch, Optical Properties of Silver Iodide Crystals, Phys. Stat. Sol. (to be published April 1971).

Suri, S. K., H. K. Henisch and J. W. Faust, Jr., Growth of β-AgI Single Crystals in Gels, J. Crystal Growth 7, 277 (1970).

Takamori, T., R. Roy and G. J. McCarthy. Observations of Surface Nucleated Crystallization in Memory-Switching Glasses, J. Appl. Phys. March (1971).

Takamori, T., R. Roy and G. J. McCarthy, Structure of Memory-Switching Glasses, I. Crystallization Temperature and its Control in Ge-Te Glasses. Mat. Res. Bull. 5, 529 (1970).

White, W. B. and G. J. McCarthy. Optical Spectra of Chromium, Nickel and Cobalt-Containing Pyroxenes. Am. Mineral. (Jan. 1971).

Part 2: RESEARCH RESULTS ON GLASS STUDIES

2.1 ULTRAHOMOGENEOUS GLASS

This work continues the approach essentially developed at Penn State over a 20 year period of "chemical-mixing" to achieve very high degrees of homogenization in inorganic multi-component systems. It is gratifying to report the recent increase in industry research activities both here and abroad in our methods.

(a) Preparation of Silica Glass from Amorphous Silica
(G. J. McCarthy and R. Roy)

Silica is the basic glass former in laser host glass formation. This study is being conducted into the feasibility of using several forms of amorphous silica to form silica "glass" at relatively low temperatures. The silica starting materials include desiccated gels from Ludox tetraethyl orthosilicate (TEOS), Cab-O-Sil and silicic acid. Formation by hot pressing (600° + 1000°C; 100 + 4 atmospheres) is being compared with standard firing (1000° - 1500°C) of samples cold pressed over a wide pressure range (100 - 40,000 atmospheres). The products are examined for crystallinity by X-ray diffraction and for index of refraction and density by standard techniques. X-ray amorphous opaque compacts with the best mechanical strength to date have been obtained from cold pressed TEOS after very rapid heating cycles. Hot pressing with relatively long heating cycles (2 hours) gives products which are partially crystalline (tridymite and cristobolite). Shorter heating cycles are being tried.

(b) Determination of Class Structure by Raman Spectroscopy

(W. B. White, G. J. McCarthy and J. McKay)

Raman scattering from glass is generally weak. Broad bands at low frequencies are related to the specific heat of the material, and somewhat sharper bands at high frequencies relate to localized vibrations of structural units. This method of glass characterization, however, has the distinct advantage that measurements can be made on bulk specimens of glass, contrary to infrared spectra which must be measured (in general) on powders.

The initial study has been concerned with glasses with compositions in the system Na_2O-B_2O_3 with specific reference to the so-called "boron anomaly." Raman spectra have been measured with a Spex Ramalog spectrometer using an ionized argon laser source. The spectra consist of some 6 to 8 broad bands between 200 and 1500 cm^{-1} and one narrow band that occurs near 77 cm^{-1} in high alkali glasses. A new narrow band at 807 cm^{-1} appears at the boron anomaly, making a doublet at less than 16 m% alkali. Only the 807 cm^{-1} band persists in B_2O_3 glass.

A new discovery, very important to glass characterization, is that the Raman spectrum appears to be very sensitive to crystallization. Even slightly devitrified glasses give rise to many sharp lines in the low-frequency region, and these lines appear in the Raman spectrum before characteristic crystal patterns appear in the X-ray powder patterns.

2.2 RADIATION-HARD DEVICES

(a) Hydrogen Impregnation of Glass

(D. M. Roy, S. P. Faile, L. N. Mulay and R. DiSalvo)

Hydrogen impregnation of glasses, usually accomplished at elevated temperatures and pressures, causes resistance to the usual darkening and coloring effects caused by neutron, proton and gamma radiation. The sug-

gested mechanism for radiation protection in silicate glasses may be expressed as the following: reaction of the radiation-produced color center (trapped hole + electron) with hydrogen to produce Si-OH and Si-H groups. The Si-OH and Si-H frequencies are identified in the IR spectra, and the usual visible and UV absorption maxima caused by radiation-produced defects are absent.

We are attempting to further characterize certain hydrogen-impregnated glasses by NMR. In preliminary experiments it was found that the equipment available was insufficiently sensitive to detect the hydrogen resonance when up to 5 mole % hydrogen was present in silicate glasses. Current efforts are directed toward synthesis of hydrogen-impregnated boron-containing glasses. It is expected that the B^{11} resonance will be sensitive to the effect of hydrogen present in large concentrations, and to the changes caused by subsequent irradiation of these glasses. Attempts at synthesizing samples with higher gas content (eight to ten mole percent may be necessary) have resulted in leakage problems in the high pressure apparatus and gas exsolution on quenching, which we are currently attempting to solve. Continued effort is being made to increase the sensitivity of the instrumentation. In the meantime, the frequency of the present NMR apparatus has been converted so as to pick up the boron resonance, and success in this area appears likely. Most current efforts are being directed toward this goal.

(b) Effect of Oxygen on the Structural Behavior of Ge-Te Glasses

(T. Takamori, G. J. McCarthy and R. Roy)

In many studies, chalcogenide glasses for switching devices appear to be prepared less carefully than those for infrared windows as far as oxygen inclusion is concerned. We have examined the effect of controlled oxygen

additions on the structure and crystallization behavior of Ge-Te glasses. Additions of oxygen up to 0.5 atomic % significantly affected the ability of the melt to wet its container, the extent of the glass forming and the microheterogeneous nature of the glass structure. What was more interesting was that the oxygen addition was found to change drastically the compositional dependency of the two-step crystallization described in the last report. Thus in many cases oxygen is an important, though often neglected, component of memory switching glasses.

(c) Sputtered Ge-Te Films

(R. Messier and R. Roy)

Thin films have been prepared from targets made of pressed powders of the two elements. Deposition rates ranged from 75 to 1300 Å/min. The preparation and characterization were related to sputtering variables such as rf power, deposition rate, sputtering gas pressure, substrate-to-target distance and effective film temperature. Vapor-deposited non-crystalline solid (VDNCS) films were obtained at all compositions in the binary system as opposed to the very limited glass forming regions for the same materials prepared by splat-cooling and water quenching methods. Only under certain conditions were the as-deposited films polycrystalline. The compositions of the sputtered films were analyzed on the electronprobe and found to be very close to that of the target material with a slight (maybe significant) shift toward the Te end of the binary diagram.

DTA and resistance-temperature experiments were conducted on the various compositions throughout the glass forming region which extends from pure Ge to at least 95 at.% Te. The crystallization temperatures of the films have been shown to be highly reproducible and sensitive to the VDNCS

"structure." At compositions 70 to 95 at.% Te and 30 at.% Te two-stage crystallization was observed in which the elemental phase - either Te or Ge - crystallized first, followed in both cases by GeTe crystallization. All other composition films displayed single stage crystallization in which two phases, either GeTe + Te or GeTe + Ge, crystallized simultaneously. The possible existence of a compositional non-uniformity in the structure of these sputtered films is indicated from the data on two-stage cyrstallization; and clearly and easily distinguishes them from splat cooled or conventional glass films.

One paper on the preparation and characterization, and a second paper on the thermal behavior of sputtered films in the Ge-Te system have been prepared for publication.

(d) Generalization of the Concept of the Crystallization Temperature of Glasses

(T. Takamori and R. Roy)

Studies of the value of crystallization temperature of glasses as a reproducible compositional and structural parameter have been expanded to include several other systems in which glass formation is difficult and crystallization at elevated temperatures is rapid. The systems include $BaO-TiO_2$, $Y_2O_3-Al_2O_3$, $SiO_2-Al_2O_3$ and $CaO-Al_2O_3$. Glasses have been obtained by splat cooling or other rapid quenching techniques. Preliminary results have shown that these glasses do indeed have a characteristic crystallization temperature, that they crystallize rapidly enough to be measured by DTA, and that this crystallization temperature varies as a function of composition. This increased understanding of crystallization of glass derived from this study should contribute to the structural analysis and optimization of various glass technologies.

Part 3: RESEARCH RESULTS ON MATERIALS PREPARATION

3.1 MATERIALS FOR IR DETECTION AND COMMUNICATION DEVICES

(a) Materials Based on CdF_2 (M. P. O'Horo and W. B. White)

Trivalent rare-earth-doped CdF_2, when heated in metal vapor, is found to have unusual electrical and optical properties for such a strong polar material. In the investigation of the crystal chemistry of this system and its possible relation to the properties it will be instructive to look at the properties of doped solid solutions of CdF_2 with other fluoride systems such as CaF_2, and especially those with filled d bands such as ZnF_2, HgF_2, PbF_2 and BiF_3. For both the electrical and optical measurements single crystals are necessary. In order to know the stability range of solid solution crystals, binary phase diagrams of CdF_2 and the above systems were determined.

The phase diagrams were determined by quench methods, DTA, and x-ray powder diffraction. In the quench method the compositions were pressed into pellets, heated either in vacuum or flowing argon until equilibrium was reached, and then rapidly quenched by dropping them into ice water. The samples were then examined with an x-ray powder diffractometer to determine the phases present and the lattice parameters. All of the DTA experiments were on a duPont 900, in a flowing argon atmosphere. We found it necessary to use graphite crucibles since the fluoride melts attack Pt and ceramic materials. From the DTA data the liquidus and solidus curves were obtained.

(i) CdF_2-CaF_2 System: This system shows complete solid solution with a narrow liquidus curve. There is some uncertainty in the melting temperature of CaF_2; our results indicate 1370°C.

(ii) CdF_2-ZnF_2 System: A simple two-phase eutectic exists, with a fluorite solid solution region on the CdF_2 side and a rutile solid solution region on the ZnF_2 side. At 700°C the CdF_2-ZnF_2 solid solution was ∿15m%. Above 80m% ZnF_2 it was difficult to determine the liquidus and solidus due to the presence of ZnO, which probably resulted from absorbed water in the ZnF_2.

(iii) CdF_2-PbF_2 System: Complete fluorite solid solution exists above 500°C, with a minimum in the miscibility gap at ∿60m% PbF_2. Below 500°C the kinetics of the system were too slow for equilibrium to occur in a reasonable amount of time. PbF_2 has an α (orthorhombic) structure below 375° and a β (fluorite) structure above. The phase transition $\alpha \rightarrow \beta$ seems to be affected by the inclusion of CdF_2 into PbF_2; it decreases by 30°C up to 30m% CdF_2 in PbF_2 and then remains constant.

(iv) CdF_2-BiF_3: This diagram is still incomplete. However, at 500°C and 600°C, solid solution extends up to 40m% BiF_3 in CdF_2.

(v) CdF_2-HgF_2: Investigations of this system are still in progress. It has not as yet been possible to keep HgF_2 from decomposing and evaporating above 450°C before a solid state reaction with CdF_2 can occur. CdF_2-HgF_2 mixtures are now being heated for long times below 400°C, in hopes a solid state reaction may occur and then permit investigation of the system at higher temperatures.

(b) Bismuth Titanate Ferroelectrics* (R. E. Newnham)

Electro-optic applications have revived interest in a number of ferroelectrics, including the bismuth titanate family. The unique optical properties of $Bi_4Ti_3O_{12}$ have prompted device proposals for optically read computer memories and for bistable light gates and display elements.

The generalized chemical formula of the bismuth titanate family is

$$M_{n+1}R_nO_{3n+3}$$

where

M = Bi, Pb, Na, K, Sr, Ca, rare earths . . . ,

R = Ti, Nb, Ta, Fe, Ga, Cr, W . . . ,

and n = 1, 2, 3, 4, 5 . . . .

The crystal structures consist of Bi_2O_2 layers interleaved with $M_{n-1}R_nO_{3n+1}$ layers containing n perovskite-like units. Most, if not all of these compounds are ferroelectric with high transition temperatures and large spontaneous polarization.

Considerable progress on the preparation and structures of these compounds has been made during the report period. Because of the intense interest in $Bi_4Ti_3O_{12}$ itself, a number of other three-layer compounds have been prepared, including $BaBi_3Ti_2NbO_{12}$, $BaBi_3Ti_2TaO_{12}$, $PbBi_3Ti_2NbO_{12}$, $SrBi_3Ti_2NbO_{12}$, $SrBi_3Ti_2TaO_{12}$, $Sr_2Bi_2TiNb_2O_{12}$, and $Sr_2Bi_2TiTa_2O_{12}$. Their existence was verified by x-ray diffraction powder patterns which yielded R factors ranging from 5 to 15%. Transition studies are now in progress.

The compounds Bi_3TiNbO_9 (n=2), $Bi_4BaTi_4O_{15}$ (n=4), $Bi_5FeTi_3O_{15}$ (n=4), and Bi_2WO_6 (n=1) were grown from the melt. Stoichiometric mixtures of the

*This work is partially sponsored by the Advanced Electronics Devices Branch, Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio.

oxides were placed in a covered platinum crucible, soaked at a maximum temperature of 1250°C over night, and then cooled with the furnace. The crystals grown from the melt were small with barely enough surface area to electrode the major faces. The compound $SrBi_2Ta_2O_9$ (n=2) was grown by melting $SrCO_3$, Ta_2O_5 and excess Bi_2O_3 in a platinum crucible and cooling at a rate of 5°C/hr. The crystals of $SrBi_2Ta_2O_9$ grown in excess Bi_2O_3 were large, rectangular plates measuring 5mm on an edge.

From x-ray examination of these and other crystals of 1-, 2-, 3- and 4-layer compounds, it is found that in the materials so far examined,

(1) All structures with an even number of perovskite sheets (2,4) have space group $A2_1am$ and exhibit two-phase transitions: one first order, one probably second order, before becoming tetragonal.

(2) All structures with an odd number of perovskite sheets (n=1,3) have space group B2cb and exhibit only a single higher temperature phase change. X-ray tests are insensitive to the slight monoclinic distortion of $Bi_4Ti_3O_{12}$.

Crystal structure refinements of $Bi_4Ti_3O_{12}$ and Bi_3TiNbO_9 are nearing completion.

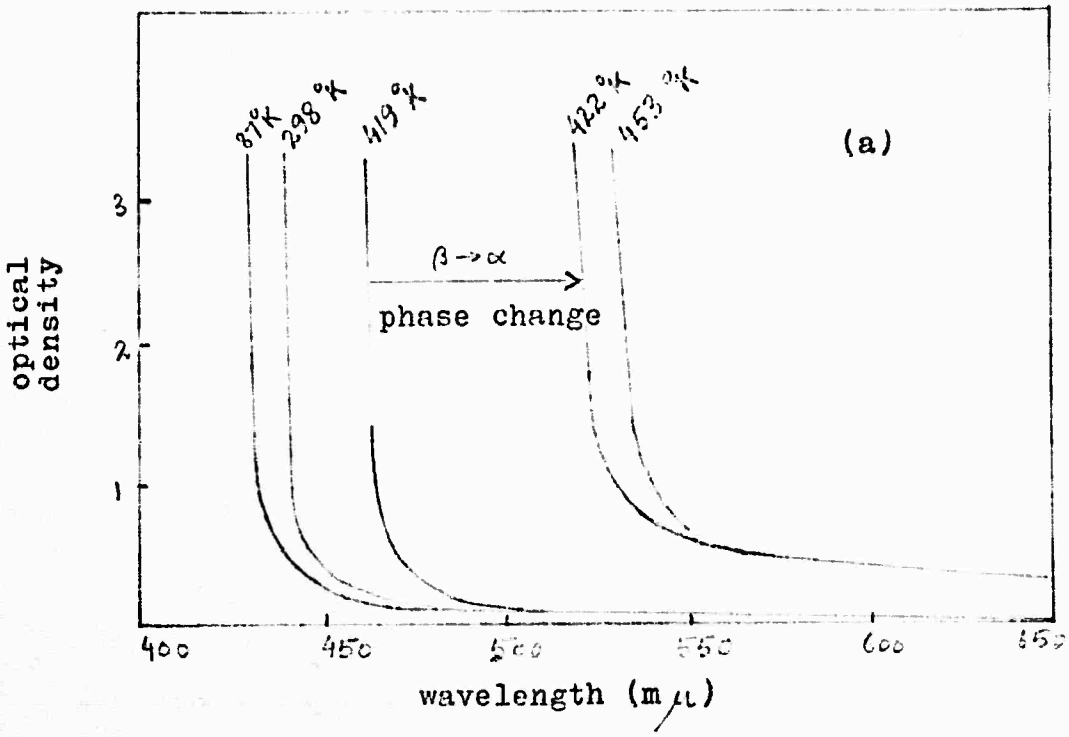
(c) Silver Iodide Crystals (H. K. Henisch and S. Suri)

The work has been concerned essentially with the optical and electrical characterization of the gel grown β-AgI single crystals (pure and copper-doped) for which the growth procedures have been perfected, as mentioned in the last report. An account of the growth work is now in print.* The material is of special interest because of its potential application as an ionic semiconductor and as a crystalline material used for cloud seeding. It is believed that the crystals used for the present investigation are of a quality not previously available.

Optical characterization involves measurements of the optical absorption edge, its temperature dependence, anisotropy and the effect of doping. The temperature range spans the β-α phase transition. Cathodoluminescence and photoluminescence have also been studied and interpreted in terms of band and defect structure. Typical data are shown in Fig. 1. An extensive paper on this topic has been prepared for publication.*

It has long been known that microcrystalline assemblies of AgI have remarkable voltage-generating properties when deformed. Whether these arise from bulk properties or intergranular contacts has remained unclear. Experiments are in progress with the object of ascertaining this by comparative tests on single crystals. In this connection it has been found that metallic contacts on AgI show a variety of complicated photo-effects, and these are also under investigation. The results available to date suggest a tentative interpretation in terms of the movement of charged dislocations, initiated by localized surface strains.

*See list of publications in Part 1 of this Report.



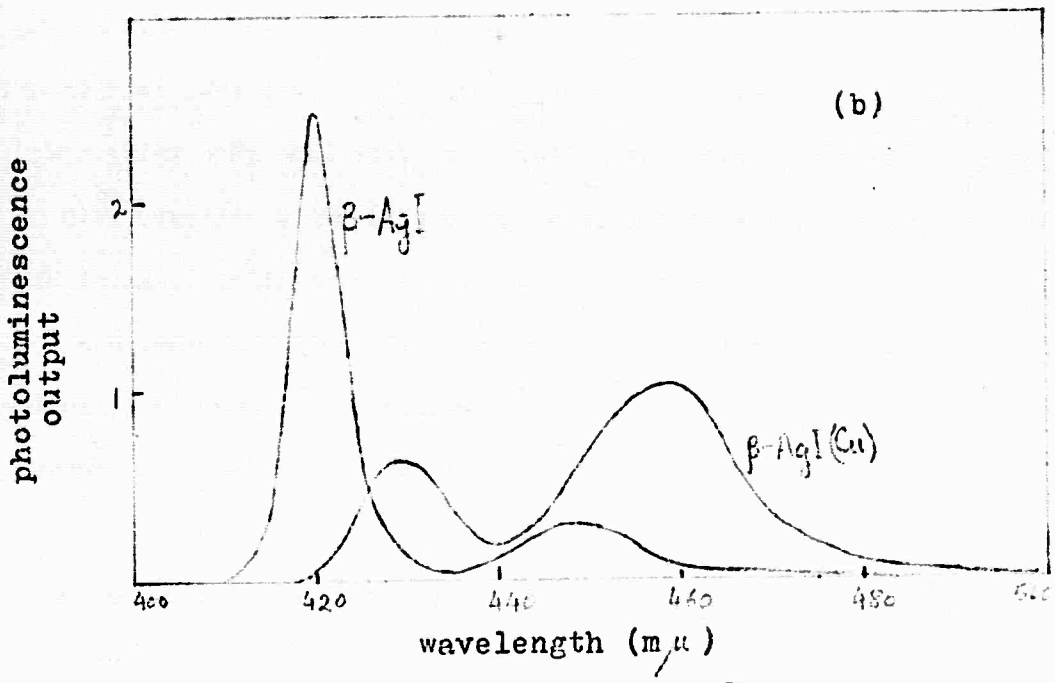


Fig. 1. Optical data for gel-grown AgI

(a) absorption spectra
(b) photoluminescence spectra at 100°K

3.2 MATERIALS OF OPTICAL AND ELECTRONIC INTEREST

(a) Vapor Phase Growth

Our increased effort in the area of vapor phase growth of crystalline materials has been in thin film preparation and the growth of bulk crystals. The thin films have been prepared by sputtering techniques [see section 2.2(c)], and by utilizing a laser beam for vaporizing the source materials for the films. We have just begun studying the use of vapor phase reactions in the growth of bulk crystals of oxides and other materials.

(i) Thin Film Growth (B. E. Knox): The newest method of preparing thin films for study utilizes a laser beam as an energy source for the vaporization of materials to be incorporated in the film. Unique films can be prepared by this technique, since large structural units appear in the vapor as a result of laser-solid interaction. Thus a hot substrate is not necessary in order to obtain crystalline films (for some materials). We have been actively working at the preparation of bismuth titanate thin films, but so far have only been able to produce crystalline films of Bi_2O_3. Iron oxide films of any type have eluded us so far, but the laser has produced very interesting melts from these materials. Germanium telluride films have also been prepared, and thus far they have all been amorphous. Other materials are currently being studied.

(ii) CdO Crystals (K. Fischer and K. E. Spear): In a recent effort to expand our research in the area of vapor phase crystal growth, we have started a project to grow very pure CdO and NiO by vapor phase reactions. Our experimental work till now has been on CdO.

The research has centered around establishing the experimental parameters that determine the quality, size, and morphology of CdO crystals produced by vapor phase reactions. Thus far we have produced epitaxial-type layers, dendritic growth, needles, and many-faceted bulk crystals with volumes of 50 to 150 mm^3. The natural faces in these latter crystals appear to have a very high degree of perfection. We are continuing to explore changes in experimental parameters that will result in the growing of even larger, more perfect crystals.

(b) Refractory Optical Host Materials

The present research was recently started in an effort to find and prepare materials of optical and electronic interest that can be used at high temperatures. This limited effort has centered around silicates, because of their potentially useful optical properties, and around rare earth borides, because of their interesting electronic properties.

(i) Growth of Silicates (R. Mohler, W. B. White): A new aspect of crystal growth, begun only recently, is the preparation of silicates. Curiously enough, little is known about silicate crystal growth except for quartz. Silicates of high optical quality seldom occur in nature and their optical properties are largely unknown. Many space groups are represented, the silicate host has a high band gap, and the materials are both refractory and stable under a variety of ambients. It would, therefore, be of interest to investigate the growth process as a function of silicate polymerization, and to then examine their potentially very interesting optical properties.

Our initial experiments have been with the growth of willemite, an orthosilicate, Zn_2SiO_4, by hydrothermal methods. Experiments thus far

have been with NaOH, KOH, and RbOH-containing aqueous solvents in the pressure range of 0.7 to 1.0 kbar. Willemite needles up to several mm in length have been obtained from KOH and RbOH solvents. Transport is not good and more effective solvents are being sought.

(ii) Preparation of Borides (G. Solovyev, E. Imperato and K. E. Spear): Metal borides, including the rare earth borides, are a group of refractories which in general have high thermal and electrical conductivity, great hardness, and chemical inertness. Lanthanum hexaboride has the best thermal emission properties known. Although potentially very useful materials, the rare earth-boron systems have been explored very little. Expected compounds not yet discovered in these systems may have even more useful properties. Many unexplainable discrepancies exist in reports on RE-B systems, but most are probably related to methods and materials used in preparation, and to incomplete characterization of the products obtained. The present work was begun in an effort to clear up some of these uncertainties and in a search for new materials. These synthesis and characterization studies will hopefully yield new methods for preparing both single and polycrystalline materials of high quality, suitable for definitive physical property measurements.

Samarium boride samples are being prepared by arc-melting mixtures of the elements, and the phase equilibria of the system is being investigated by both x-ray and metallographic techniques. Two phases reported previously for this system, SmB_4 and SmB_6, were identified and a new boron-rich phase with a composition of about SmB_{80} was discovered. Melting temperatures and behavior, eutectic compositions, thermal stability, microhardness, and lattice parameters are also being investigated in the present program. A similar investigation of the gadolinium-boron system has just begun.

(c) Hydroxyapatite (D. M. Roy and S. Sawatani)

Phase equilibria in the system $CaO-P_2O_5-H_2O$ are under investigation relevant to the crystallization and growth of hydroxyapatite. The equilibrium $CaHPO_4 \cdot 2H_2O$ (brushite) = $CaHPO_4$ (monetite) + $2H_2O$ has been determined as a function of pressure, varying from 25°C at 1 atm. to 43°C at 15,000 psi. The pT curve established for the equilibrium explains the erratic behavior of brushite under ambient conditions.

A preliminary examination of equilibria involving hydroxyapatite and compatible phases at elevated temperatures and pressures in the system $CaO-P_2O_5-H_2O$ has been made. Apatite phases of varying stoichiometry have been synthesized (usually in equilibrium with a second crystalline phase + vapor) from mixtures containing controlled concentrations of H_2O added to $3CaO \cdot P_2O_5$, $2CaO \cdot P_2O_5$ and $3CaO \cdot P_2O_5$ - $Ca(OH)_2$ mixtures. The best crystals grown to date are needle-shaped ranging up to several mm. length, produced from $3CaO \cdot P_2O_5$ - $Ca(OH)_2$ - H_2O ternary mixtures. Electron probe analyses indicate a close approach to the stoichiometric composition $Ca_{10}(PO_4)_6(OH)_2$ for certain of these crystals. Experiments are continuing to determine the range in stoichiometry of the apatite crystals as a function of temperature, pressure and batch composition, and to establish reproducible parameters for optimum growth of the desired crystals.

(d) Growth of Single Crystal Calcite (J. F. Balascio and W. B. White): Clear calcite rhombs up to 3 mm on an edge have been grown hydrothermally from K_2CO_3 - H_2O solutions. It appears necessary to keep the reaction pressure in the range of 1.7 kbar or above to avoid the formation of the hydrated double salt phase, $3K_2CO_3 \cdot 2CaCO_3 \cdot 6H_2O$. Rough phase relations have been mapped and the double salt phase does not appear above 1.7 kbar at any

temperature. In contrast, growth of calcite does not take place from Na_2CO_3 solutions under any conditions examined, while growth is obtained from Rb_2CO_3 solutions under a wide range of conditions.

Some attempts have been made to grow calcite by Czochralski pulling from Li_2CO_3-$CaCO_3$ solutions. The viscosity of the lithium carbonate flux is too high for effective pulling techniques. Experiments with LiCl additives to lower the viscosity are now underway.

Part 4: RESEARCH RESULTS ON MATERIALS CHARACTERIZATION

4.1 CHARACTERIZATION OF SINGLE CYRSTALS WITH A DOUBLE CRYSTAL SPECTROMETER

(A. S. Bhalla and E. W. White)

(a) Double Crystal Spectrometer (DCS)

The double crystal spectrometer (DCS) constructed under earlier Air Force funding has been evaluated for its application to problems of single crystal characterization. The instrument can be operated under stable temperature conditions in air or in vacuum. Bragg angles are scanned in steps of one second of arc with an accuracy of $\pm$ 0.1 second of arc. The high resolution of the instrument was tested by using the (111) reflection on silicon, germanium and various other crystals. The DCS proved to be highly stable, thus giving good reproducibility of measurements when tested with (200) reflection on NaCl single crystals using CrKα radiation. Various parts of the instrument were analyzed individually for accuracy in measurement and a total error $\pm$ 0.34 seconds of arc (which could be eliminated also) was estimated due to the aggregate effect of all parts of the apparatus.

A very simple method has been developed for aligning the DCS to within $\pm$ 2 seconds of arc with the help of optical flats. Some criterion for cutting crystals parallel to any diffracting plane, with an accuracy of $\pm$ 10 seconds of arc, were established and many sets of silicon, NaCl, Germanium etc., were thus prepared.

The DCS, thus built and tested for its resolving power, stability, reproducibility, accuracy and precision in measurements, was used in various problems of materials characterization. Some of the studies made and conclusions drawn are given in the following sections. The results obtained had

very high accuracy and much confidence in the measurements and thus showed the capability of DCS in dealing with the precision studies in the field of materials science.

(b) Precision lattice parameters

Measurements were made on crystals of silicon, germanium, quartz, β-silver iodide and gadolinium molybldate. The results on silicon (obtained from Dr. R. L. Barns) were quite close (1 ppm) to the value reported by Barns. Thus, DCS was successfully used for precision lattice parameter measurements. Moreover, the measurements were also made with SCS part of the DCS and results were in agreement with the values of DCS.

DCS was also used for measuring $\Delta\theta$ for the determination of linear coefficient of thermal expansion of silicon and germanium in the temperature range of 25°C-41°C. The value of $\alpha_{si} = 2.327 \times 10^{-6}{}^{\circ}C^{-1}$ and $\alpha_{Ge} = 5.722 \times 10^{-6}{}^{\circ}C^{-1}$ obtained were very close to the dialatometric measurements ($\alpha_{si} = 2.33 \times 10^{-6}{}^{\circ}C^{-1}$ and $\alpha_{Ge} = 5.75 \times 10^{-6}{}^{\circ}C^{-1}$). Thus the method proved to be a very simple, accurate and rapid technique. Also it does not require precise lattice parameter measurements at extreme temperature.

(c) Crystal Perfection

Perfection of the crystals of silicon, germanium, zinc sulphide (sphalerite), gallium arsenide, silver chloride and bromide was studied with respect to their dislocation densities (ρ). The values of ρ obtained by x-ray method with DCS were quite higher as compared to those obtained by etch pit technique when considering specimens with large dislocation densities. At low dislocation density limits the correlation was very satisfactory. The reasons for the observed differences between the two techniques are probably:

(i) unavailability of suitable dislocation revealing etchants

(ii) small dislocation pits merge into the bigger pits when ρ is large

(iii) dislocations at angles >30° do not show in microscopic observation of etch pits.

(iv) screw dislocations may not show by etching

Thus, DCS utilized for this purpose seemed to be quite reliable for estimating dislocation densities in single crystals. One of the important applications of this technique was found to be in estimating the dislocation densities of Cu halides and β-AgI where suitable etchants were not available. Typical values of ρ, 10^6 - $10^7/cm^2$, were obtained for these crystals.

Growth misorientation contents of crystals were studied from the peak broadening of DCS diffraction peaks. Germanium crystals with misorientations as low as 10-20 seconds of arc were studied.

(d) Crystallographic Polarity

Non-centrosymmetric crystals such as those having the zinc-blende and wurtzite structures (including crystals in $F\bar{4}3m$, $P6_3mc$ & $R3m$ space group) exhibit crystallographic polarity. Halides of Cu and β-AgI crystallize with zinc blende and wurtzite structures, respectively. Studies were made on these crystals for crystallographic polarity determinations and the following results were concluded:

(1) The Double Crystal Spectrometer (DCS) measurements of intensities of various reflections from (111), $(\bar{1}\bar{1}\bar{1})$ and (00.1), $(00.\bar{1})$ surfaces of Cu-halides and β-AgI, respectively, showed that the (111) or (00.1) plane in these structures consists of cations, whereas the $(\bar{1}\bar{1}\bar{1})$ or $(00.\bar{1})$ consists of anions. Also the (00.1) face in β-AgI showed etch pits, whereas $(00.\bar{1})$ did not show any etch pits on the surface.

(2) DCS measurements showed that the x-ray peak width from (111) or (00.1) type planes is larger than the respective peak width from $(\bar{1}\bar{1}\bar{1})$ or $(00.\bar{1})$ type planes for the same order of reflection.

It is important to note that very small crystals (0.5 - 1.0 mm) could be used for direct measurements of crystallographic polarity.

(e) Li-Drifted Germanium

Some samples of pure, gallium-doped, and lithium-drifted germanium were tested for surface damage caused by doping or drifting of lithium. It was concluded that maximum surface damage occured while drifting the lithium into the samples. Such samples showed a large amount of growth misorientation and surface damage. A small amount of surface damage was also found on some doped samples. No growth misorientation features were found on pure germanium.

(f) Piezoelectric Constants

By noticing the small changes in Bragg angle, very small uniform strains $\sim 10^{-5}$ are measureable, which made it feasible to determine the longitudinal piezoelectric coefficient directly. Some such measurements were made on quartz and the value of $d_{11} = 6.94 \times 10^{-8}$ cgs thus obtained was very close to the various accepted values for d_{11} ($6.7 - 7.0 \times 10^{-8}$ cgs).

4.2 CHARACTERIZATION OF RESIDUAL STRAIN

(H. McKinstry)

(a) Alumina

X-ray diffraction peaks have been obtained from hot pressed samples of Al_2O_3. The samples were cut to size for use on the diffractometer. Part

of the samples were examined as cut. Others were ground and then chemically polished in borax for twenty five minutes at 825°C in order to remove the surface damage. The strain and coherent domain size of both sets of samples are being examined by the Warren-Averbach method.

(b) Temperature Diffuse Scatter

The effect of temperature diffuse scatter is not usually considered in x-ray diffraction experiments designed to measure strain and coherent domain size. It is known that the thermal vibration of the atoms in a material produces a diffuse peak which adds to the regular Bragg peak. Ramachandran and Wooster (1951) have given a general expression for the temperature diffuse scatter which applies to a crystal with any symmetry. Temperature diffuse scatter from cubic powders has been thoroughly discussed by Warren (1953), Paskin (1958 & 1959) and Chipman and Paskin (1959a & b). An expression for the temperature diffuse scatter is being added to a computer program which simulates x-ray diffraction peaks by a convolution of geometric broadening factors. In this way it will be possible to assess the effect which the temperature diffuse scatter has on measured strain and coherent domain size.

(c) PLZT

X-ray diffraction peaks are being obtained from hot pressed samples of

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Chipman, D. R. and Paskin, A., J. Appl. Phys. 30, 1992 (1959a).
Chipman, D. R. and Paskin, A., J. Appl. Phys. 30, 1998 (1959b).
Paskin, A., Acta Cryst. 11, 165 (1958).
Paskin, A., Acta Cryst. 12, 290 (1959).
Ramachandran, G.N. and Wooster, W. A., Acta Cryst. 4, 335 (1951).
Warren, B. E., Acta Cryst. 6, 803 (1953).

a lead zirconate-lead titanate solid solution containing 8 mole percent lanthanum oxide. The samples are ferroelectric with a tetragonal-rhombohedral phase transformation at 65% $PbZrO_3$. Poling the samples by the application of a dc electric field causes growth of favorably oriented domains resulting in anisotropic response to electrical and optical stimuli. The unusual electroptic properties of the lead zirconate-lead titanate ferroelectrics have given rise to much current interest. These properties have been discussed by Land and Thacher (1968).* The x-ray diffraction peaks from these samples will be used to determine coherent domain size and strain by the Warren-Averbach method. The size and strain will be measured near the tetragonal-rhombohedral phase transformation before and after poling of the samples.

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* Land, C. E. and Thacher, P. D., "Ferroelectric Ceramic Electroptic Materials and Devices," Sandia Laboratories, Research Report SC-RR-68-866, December, 1968.